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TITLE OF THE INVENTION

HYDROGEN SEPARATION USING OXYGEN ION-ELECTRON MIXED CONDUCTING  
MEMBRANES

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CROSS REFERENCE TO RELATED APPLICATIONS

This applications claims priority to United States  
10 Provisional Application Ser. No. 60/373,531, filed 4/18/02, which  
is incorporated in its entirety herein.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
15 DEVELOPMENT

N/A

BACKGROUND OF THE INVENTION

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Proton exchange membrane (PEM) fuel cells are fast  
approaching commercialization for application in the  
transportation and stationary sectors. One of the needs for  
the operation of a PEM fuel cell is that of high purity hydrogen  
25 with less than ~10 ppm of impurities such as CO. It is  
therefore expected that if PEM fuel cells are to have wide  
applications, an infrastructure to produce tonnage quantities of  
high purity hydrogen has to be available.

Presently tonnage hydrogen is produced by reformation of  
30 hydrocarbon fuel followed by the water gas shift reaction and  
pressure swing adsorption (PSA) of the CO<sub>2</sub>. The major disadvantage  
of the current process especially in reference to PEM fuel cell  
application is that the purity levels that can be attained are

hydrocarbon reformat) and steam on one side and pure steam on the other side), the reactions are:

On the syn gas side:  $\text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{e}^-$

5  $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$

On the other side:  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-}$

Oxygen ions formed through dissociation of steam through absorption of two electrons on the steam side transport to the syn-gas side where they combines with carbon monoxide and hydrogen in the syn gas to form carbon dioxide and steam and liberate two electrons. The liberated electrons transport through the same membrane in the opposite direction to the steam side to participate in the steam dissociation reaction. The gases exiting the steam side of the membrane contain a mixture of hydrogen and remnant water vapor. The water vapor present in this stream can be condensed in a condenser to result in a stream of pure hydrogen. (These reactions are discussed in more detail in relation to Figure 3.) Further, if the steam formed on the syn gas side is continuously condensed to a level where carbon deposition does not occur in the membrane reactor, the reaction is forced to the right, resulting in a higher conversion of the syn gas to hydrogen. Although in most instances it may not be economically favorable to condense the steam mid-process on the syn gas side, in principle it can be achieved if higher conversion rates are desired.

The membranes used here are solid state ceramic membranes, which are very dense and non-flexible. Their thickness generally ranges from about 5-10  $\mu\text{m}$  up to about 1-3 mm. These membranes separate components on the basis of ionic conductivity characteristics, not on the basis of molecular size. The temperature at which these membranes are effective are generally above 500C, usually about 800-1000C. The use of the solid state

syn-gas application. Thus stability issues with respect to LSCF are much less of a concern in the method disclosed herein.

Another example of a single phase membrane possessing ionic and electronic conductivities is yttria stabilized zirconia (YSZ) doped with an oxide chosen from:  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{Cr}_2\text{O}_3$  or other transition metal oxides. Yet another example is undoped  $\text{CeO}_2$  or  $\text{CeO}_2$  doped with an oxide chosen from  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{Cr}_2\text{O}_3$  or other transition metal oxides.

In two-phase membranes, the concept is to separate the functions of ionic and electronic conduction. Any oxygen ion conductor and any metal can be chose for this purpose. Examples are a two-phase mixture of YSZ (ionic conductor) and Pd (or one of Pt, Ni, Ag, Au). Another example is a mixture of  $\text{RE}_2\text{O}_3$  doped  $\text{CeO}_2$  (ionic conductor, where  $\text{RE}=\text{Y}$ ,  $\text{Yb}$ ,  $\text{Sc}$ , or  $\text{Gd}$ ) and Pd (or one of Pt, Ni, Ag, Au). Other examples of two-phase mixed conductors include LSGM ( $\text{La}_{1-x}\text{Sr}_x\text{Mg}_y\text{Ga}_{1-y}\text{O}_3$ ) + Ni or LSGM + Pd. In the case of LSGM, stability is not expected to be a problem since it is already being developed as an electrolyte for solid oxide fuel cells (SOFCs) where highly oxidizing atmosphere (air) is expected to prevail on the cathode side and a highly reducing atmosphere ( $\text{H}_2$  and/or  $\text{CO}$ ) is expected to prevail on the anode side.

Other dense particulate composites of ionic conducting phases and electronically conducting phases can also be used. Mixtures of any 2 or more of the above membrane materials can also be used to fabricate the membrane.

The most preferred membranes for hydrogen purification are  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$  + Pd. The most preferred ratio is 50% Pd and 50%  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ , although other ratios are possible.

Thin membranes generally allow efficient transport across them. (The optimum thickness for the membranes used herein has been found to be approximately 5-10 microns (5-10  $\mu\text{M}$ ).) However, these membranes are quite fragile. However, as membranes get

inner tube (and passing over the insides of the membrane) and syn gas passing over the outside of the membrane, is also possible.

A bench scale apparatus is shown in Figure 4. The membrane 30 is sealed between cut ends of two alumina tubes (31 and 32).  
5 Between the membrane and the ends of the tubes is placed an o-ring for sealing the membrane to the tubes. This frequently is a gold o-ring 35 that melts and forms the seal. A smaller diameter tube 33 is inserted into the syn gas side of the membrane (which is closed from the atmosphere with a stainless steel manifold 37) to  
10 carry the syn gas to the membrane, while the purified hydrogen gas is removed from the opposite side of the membrane via another tube 34. The entire apparatus is heated to 800-1000C with furnace heating elements 36.

A larger scale apparatus for hydrogen purification is very  
15 similar to that used for oxygen purification, as shown in Schwartz, U.S. Patent No. 6,033,632.

Figure 5 shows the degree of conversion versus the flow ratio. The degree of conversion is the ratio of the hydrogen flow at the exit on the steam side of the membrane shown in Figure 2 to  
20 the total flow of carbon monoxide and hydrogen introduced into tube 10 in Figure 2. The flow ratio is the ratio of the total inlet steam on the steam side of Figure 2 to the total flow of carbon monoxide and hydrogen introduced into tube 10 in Figure 2.

Hydrogen on the steam side exit can be simply recovered by  
25 passing the steam and hydrogen mixture through a condenser and condensing the steam.

It is also possible to enhance the rate of hydrogen separation by partially condensing the steam formed on the syn gas side mid-process. Although this may not be economically favorable  
30 in principle it is possible to achieve further enhancements in hydrogen separation rates through this process.

Alternate processes for hydrogen purification utilize the sorption enhanced reaction, which yields hydrogen with much

Silicone rubber gaskets **38** are placed between the stainless steel manifolds and the alumina tube to create a gas tight seal. Alumina tubes **42** carry components into and out of the 2 chambers. The entire apparatus consists of the stainless steel manifold,  
5 silicone rubber gaskets, dense alumina tubes, gold o-rings and pellet sample, kept under moderate pressure using a spring loading mechanism **43**.

During measurement, a mixture of Ar (carrier gas) and water vapor is fed into one side of the membrane **39** through a port  
10 machined into one of the stainless steel manifolds. Simulated syn gas containing  $H_2$ ,  $CO$ ,  $H_2O$  is fed to the opposite membrane side through a port **40** machined into the other stainless steel manifold. By measuring the Ar and steam mixture flow rate and the gas that exits at the exit port on this side of the membrane, the  
15 hydrogen permeation rate can be measured.

#### Example 2: Making the $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3 + Pd$ membrane

To make  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$  membrane, initially precursors of lanthanum carbonate, strontium carbonate, gallium oxide and  
20 magnesium oxide are mixed in stoichiometric ratios and heated in a furnace in air in the temperature range of 1200-1400°C for a period ranging from 10 minutes to a few days. The powders thus formed are then mechanically milled in a plastic bottle using ceramic milling media (example yttria stabilized zirconia) for a  
25 period (preferably one day) in an organic solvent (preferably isopropanol). The resulting finer particle size  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3$  is well mixed with fine Pd powder obtained from Johnson Matthey. The resulting powder mixture is placed in a uniaxial die press and pressed into a pellet. The resulting  
30 pellet is then fired in the temperature range of 800-1400°C to yield the  $La_{0.9}Sr_{0.1}Ga_{0.8}Mg_{0.2}O_3 + Pd$  membrane pellet.

4. The process of claim 3 wherein said membrane is selected from the group consisting of:

strontium doped lanthanum iron cobalt oxide of the composition  $\text{La}_{(1-x)}\text{Sr}_x\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$  ;

5  $\text{La}_{(1-x)}\text{Ca}_x\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$  ;

$\text{La}_{(1-x)}\text{Sr}_x\text{Co}_{y1}\text{Fe}_{y2}\text{Ni}_{y3}\text{Cr}_{y4}\text{O}_3$  ;

yttria stabilized zirconia doped with an oxide selected from the group consisting of  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{Cr}_2\text{O}_3$  and other transition metal oxides;

10 undoped  $\text{CeO}_2$  ;

$\text{CeO}_2$  doped with an oxide selected from the group consisting of  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{FeO}$ ,  $\text{Cr}_2\text{O}_3$  and other transition metal oxides;

yttria stabilized zirconia and a metal selected from the group consisting of Pd, Pt, Ni, Ag and Au;

15  $\text{RE}_2\text{O}_3$  doped  $\text{CeO}_2$  , where RE is Y, Yb, Sc, or Gd, and a metal selected from the group consisting of Pd, Pt, Ni, Ag and Au;

$\text{La}_{1-x}\text{Sr}_x\text{Mg}_y\text{Ga}_{1-y}\text{O}_3$  and Ni;

$\text{La}_{1-x}\text{Sr}_x\text{Mg}_y\text{Ga}_{1-y}\text{O}_3$  and Pd and mixtures thereof.

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5. The process of claim 3 wherein said membrane is selected from the group consisting of:

strontium doped lanthanum iron cobalt oxide of the composition  $\text{La}_{(1-x)}\text{Sr}_x\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$ , where  $0 < x < 1$  and  $0 < y < 1$  ;

25  $\text{La}_{(1-x)}\text{Ca}_x\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$  , where  $0 < x < 1$  and  $0 < y < 1$ ; and

$\text{La}_{(1-x)}\text{Sr}_x\text{Co}_{y1}\text{Fe}_{y2}\text{Ni}_{y3}\text{Cr}_{y4}\text{O}_3$  where  $x < 1$  and  $y1+y2+y3+y4=1$  .

6. The process of claim 3 wherein said membrane is

$\text{La}_{(1-x)}\text{Sr}_x\text{Co}_{(1-y)}\text{Fe}_y\text{O}_3$ , where  $0 < x < 0.4$  and  $0 < y < 1$  .

30

7. The process of claim 3 wherein said membrane is  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3 + \text{Pd}$ .

## CLAIMS

What is claimed is:

- 5 1. A process for purifying hydrogen from a stream of reformat gases comprising:
- a. preparing a flow cell in which 2 gas flows are separated by a solid state ceramic membrane,
  - b. heating said cell to greater than 500C,
  - 10 c. passing said reformat gas and a small amount of steam on one side of said membrane and steam on the second side of said membrane, and
  - d. separating said purified hydrogen from said second side of said membrane.
- 15 2. The process of claim 1 wherein said reformat gases are selected from the group consisting of:
- (a) mixtures of carbon monoxide and hydrogen;
  - (b) mixtures of carbon monoxide and hydrogen containing small
  - 20 quantities of other hydrocarbons or hydrocarbon reformat or inert gases such as Ar, He or nitrogen;
  - (c ) by-products from the partial oxidation or steam reformation of methane;
  - (d) partial oxidation or steam methane .reformation products of
  - 25 other hydrocarbons;
  - (e) products of carbon dioxide reformation of hydrocarbons;
  - (f) products of autothermal reformation of methane and other hydrocarbons; and
  - (g) mixtures thereof.
- 30 3. The process of claim 1 wherein said membrane is selected from the group consisting of single phase and two-phase membranes.